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Oligomerisation of ethene by new palladium iminophosphine catalysts

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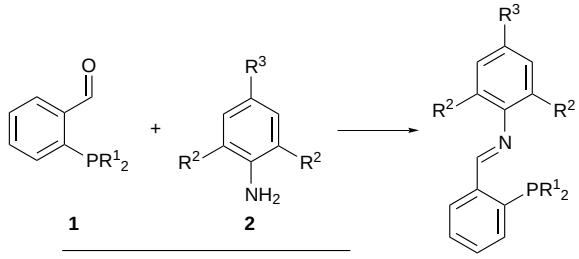
Oligomerisation of ethene in polar solvents at higher temperatures is achieved using new palladium iminophosphine catalysts and the oligomer selectivity can be controlled by the nature of the ligand substituents.

Oligomerisation and polymerisation of alkenes by early[1] and late transition metal catalysts[2] leads to important commercial products and currently much effort is devoted towards the development of more efficient and selective catalysts. Commonly, late transition metal complexes produce dimers of alkenes due to fast β-hydrogen abstraction.[3] Until now, only a limited number of oligomerisation or polymerisation reactions by late transition metal catalysts are known. An example is the ethene oligomerisation process with a nickel catalyst developed by Keim *et al.*,[4] well known as SHOP[1a] (Shell Higher Olefin Process). Recently, Brookhart and coworkers have reported on ethene polymerisation with bisimine Pd^{II} or Ni^{II} complexes in CH_2Cl_2 or toluene.[5] Furthermore, bisimine and bisphosphine Pd^{II} complexes are highly efficient in alkene/CO copolymerisation.[6] We report here new palladium catalysts based on iminophosphine ligands which result in the unexpected switch to oligomerisation of ethene in polar solvents.

Bidentate iminophosphine ligands are known to bind to Pd in a unique way: the soft P atom coordinates very strongly to Pd whereas the hard N donor is weakly bound.[7] We envisaged that these features might be exploited in tuning the reactivity of Pd complexes in alkene coupling reactions. For this purpose, we synthesised new iminophosphine ligands **3** from the corresponding amine and aldehyde[8] as shown in Scheme 1.

The catalysts were formed by the combination of the bidentate ligands **3**, $Pd(OAc)_2$ and a weakly or non-coordinating anion (X^-) for instance toluene-*p*-sulfonic acid (TsOH), *via* an anion exchange reaction. The oligomerisation reactions



1 **2**

	R^1	R^2	R^3
3a	Ph	H	H
b	Ph	Me	H
c	Ph	Pr^i	H
d	C_6H_4OMe-*p*	Pr^i	H
e	C_6H_4OMe-*m*	Pr^i	H
f	C_6H_4OMe-*o*	H	Cl
g	C_6H_4OMe-*o*	H	H
h	C_6H_4OMe-*o*	H	OMe
i	C_6H_4OMe-*o*	Pr^i	H

Scheme 1 Synthesis of **3**

performed under 20 bar ethene with these complexes gave remarkable results: at a high temperature (100 °C) and in a polar solvent (MeOH) higher alkenes were obtained (Table 1). In sharp contrast with these results, diphosphines show higher conversion rates at these temperatures, but only dimers are obtained[3d] whereas Brookhart's diimine system[5] polymerises ethene at 25 °C. In the latter case, chain transfer took place only a few times (for 0.1 mmol Pd catalyst, 45.3 g polyethylene was obtained with $M_w = 11.2 \times 10^4$), while for the new ligand system this feature was observed many times (for **3i** *ca*. 250 times).

Table 1 shows the product ratios for various iminophosphine ligands.† Increasing the steric bulk at the nitrogen donor site, results in higher molecular masses (compare entries 1 and 2 with 3 and 7 with 9). Furthermore, when more steric bulk on the phosphorus site is introduced (in the case of *o*-OMe analog **3i**) the molecular mass is increased again (compare entries 3, 4, 5 and 9). This is in accordance with observations by Brookhart and coworkers, who found with bisimine ligands, that blocking of the axial positions led to polymers with higher molecular mass.[5]

To obtain more insight into the structure of the catalyst, an X-ray analysis was performed on [Pd(L)Me(Cl)] **4** (L = **3i**),‡ which was synthesised from **3i** and [Pd(cod)Me(Cl)] (cod = cycloocta-1,5-diene). In structure **4** (Fig. 1) Pd is coordinated by N, P, Cl and a Me group in a square planar mode. Examination of the space filling model of **4** showed that one axial position of Pd is blocked effectively by an Pr^i group and one *o*-OMe group (Fig. 2). The other axial position is partly blocked by the second *o*-OMe group.

Remarkably, the activity is increased dramatically (turnover number from 250 to 1100), by replacing the two Ph groups on P by *o*-OMePh groups (Table 1, entry 8). This is due to a steric effect because no higher activity was obtained for the *p*-methoxyphenyl analogue. The catalytic activity is furthermore influenced by electronic effects in the imino donor site; in particular electron releasing groups enhance the rate. For instance by changing R^3 from Cl **3f** to OMe **3h** an increase of turnover from 150 to 800 is observed.

Table 1 PN ligands in ethene oligomerisation and percentage of products[a]

Entry	Ligand	Time/h	T.O.[b]	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}
1	**3a**	9	250	85	12	3			
2	**3b**	9	250	74	15	11			
3	**3c**	9	250	53	29	13	4	1	
4	**3d**	5	125	63	26	9	2		
5	**3e**	5	150	62	26	10	2		
6	**3f**	5	150	44	23	16	10	5	2
7	**3g**	5	500	34	26	19	12	6	3
8	**3h**	5	800	36	27	18	12	6	1
9	**3i**	5	1100	22	25	22	16	9	6

[a] 0.1 mmol $Pd(OAc)_2$, 0.11 mmol ligand, 0.21 mmol TsOH, 20 bar ethene, 50 ml MeOH, T = 100 °C (product ratio determined by GC). [b] T.O. = Turnover; mol consumed ethene/mol palladium.

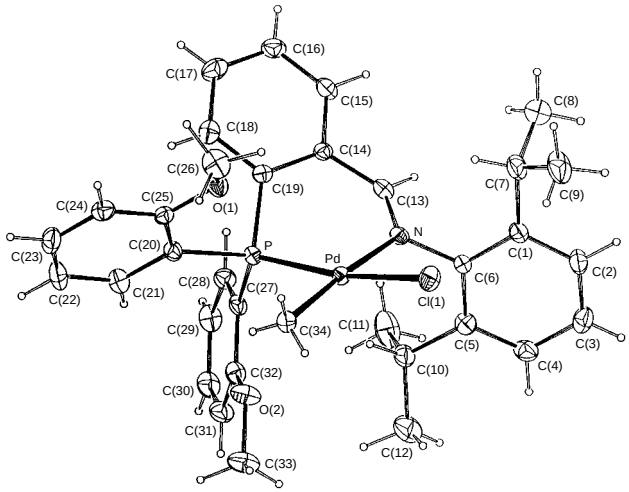


Fig. 1 Ellipsoid plot (drawn at 50% probability) of **4**, with adopted atom labelling (CH_2Cl_2 solvent not shown). Selected bond lengths (Å) and angles (°): Pd–P 2.2092(10), Pd–N 2.170(3), Pd–Cl 2.3734(11), Pd–C(34) 2.062(4); Cl–Pd–P 168.85(4), Cl–Pd–N 92.08(9), Cl–Pd–C(34) 88.29(10), P–Pd–N 89.72(9), P–Pd–C(34) 90.86(10), N–Pd–C(34) 175.08(12).

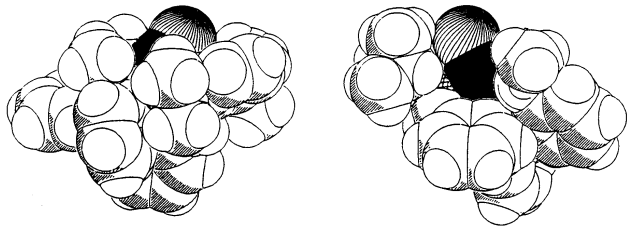


Fig. 2 CPK plots of **4** (top and bottom view, Pd = black)

A tremendous activity increase could be obtained by change of solvent. For instance, in ethylene glycol the activity increased to 1100 turnovers in 1.5 h by using ligand **3h**.

With all ligands, the molar growth factor K (moles C_{n+2}/mol C_n) is dependent on the chain length. When the chain length is higher, K decreases; for example **3i** gave $K(C_8/C_6) = 1.14$ while $K(C_{14}/C_{12}) = 0.6$ (Table 1). This suggests that chain migration takes place, giving branched alkyl fragments. This branching leads to a decreased propagation and increased termination owing to steric hindrance. This is confirmed by the observation that for longer chains, more branched products were found (Table 2). Furthermore, the isomerisation increased (K decreased) at higher temperatures [*e.g.* **3i** gave $K(C_8/C_6) = 1.46$ at 70 °C and 0.88 at 120 °C, Table 3] as well as the amount of branched products (Table 2). Decrease of the steric hindrance in the ligand, resulted also in more branched products (compare **3c** and **3i**).

Table 2 Percentage linearity of C_6–C_{12}

Entry	Ligand	T/°C	Linear C_6 (%)	Linear C_8 (%)	Linear C_{10} (%)	Linear C_{12} (%)
1	**3c**	100	92	88	83	77
2	**3i**	100	94	92	89	83
3	**3i**	120	94	89	77	76

Table 3 Product ratio (%) dependence on temperature for **3i**

Entry	T/°C	Time/h	T.O.	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}
1	70	16	650	17	24	22	17	12	8
2	100	5	1100	22	25	22	16	9	6
3	120	5	1650	32	28	20	11	6	3

In conclusion, a new palladium based catalyst system for ethene oligomerisation has been developed. Remarkable features are the excellent stability in polar solvents at high temperatures, the formation of C_6–C_{16} oligomers at these temperatures and the possibility to tune the oligomer selectivity by the iminophosphine ligands.

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Footnotes and References

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† The amount of butenes was not measured due to the volatility. Therefore, the combined C_6–C_{16} fractions are set at 100%; the relative mol percentages for the alkenes in this range are given. However, it should be noted that in case the amount of octenes is larger than the amount of hexenes, the amount of butenes is expected to be lower than the amount of hexenes.

‡ *Crystal data* for **4**: $C_{34}H_{39}ClNO_2PPd{\cdot}CH_2Cl_2$, M_r = 751.47, yellowish block shaped crystal (0.13 × 0.20 × 0.50 mm), monoclinic, space group $C2/c$, a = 38.074(5), b = 10.851(1), c = 17.661(1) Å, β = 111.10(1), U = 6807.2(1) Å^3, Z = 8, D_c = 1.467 g cm^{-3}, $F(000)$ = 3088, μ(Mo-Kα) = 8.6 cm^{-1}; 8340 reflections ($1.15 < \theta < 27.50°$; ω scan; T = 150 K) were measured on an Enraf-Nonius CAD-4T diffractometer (rotating anode, graphite-monochromated Mo-Kα radiation [λ = 0.71073 Å]). Data were corrected for L_p effects, for the linear decay (0.4%) of the intensity control reflections during 19 h of X-ray exposure and merged into a dataset of 7671 unique reflections. The structure was solved with standard Patterson methods (DIRDIF 96) and difference Fourier techniques. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. All non-H atoms were refined on F^2 (SHELXL-96) using all 7671 unique reflections, with anisotropic thermal parameters. Convergence was reached at R_1 = 0.0460 for 5757 reflections with $I > 2.0\sigma(I)$ and 421 parameters; wR_2 = 0.1065, S = 1.011 for all 7671 reflections, $w = 1/\sigma^2(F_o^2) + (0.0488P)^2 + 5.42P$. A final difference Fourier map shows residual densities between −1.11 and +0.70 e Å^{-3}. CCDC 182/690.

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